Fabrication of Dye-Sensitized Solar Cells (DSSC)
Device using Lawsonia Inermis LEAF

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Abstract

Lawsonia inermis leaves extracted in cold ethanol (A) and soxhlet ethanol extractor (B) were used as natural sensitizers for wide band-gap semiconductor (TiO₂) photoelectrochemical solar cells. The natural dye, adsorbed onto the semiconductor surface, absorbs visible light and promotes electron transfer across the dye/semiconductor interface. The DSSC sensitized by extracts A achieved up to Jsc 0.82 mAcm⁻², Voc 0.302V, FF 0.659 and η 0.349%, while for extract B sensitized cells the values determined were Jsc 0.94mAcm⁻², Voc 0.72V, FF 0.828 and η 0.677%. The characterization of the solar cells by XRD shows that the TiO₂ thin film covered substrate obtained from (A) and (B) indicate an Anatase phase and adjustment of pH shows increase in efficiency as pH decreases. A phytochemical screening performed shows the presence of flavonoids and anthraquinones, which makes effective electron transfer from the anthocyanin molecule to the conduction band of the TiO₂. This study represents a simple technique of producing a low cost environmentally friendly dye-sensitized solar cell

Keywords: Nanocrystalline TiO₂, Lawsonia Inermis, Photoelectrochemical Solar Cell, Natural Dye, Semiconductor.

Introduction

Due to the increasing energy demands and environmental concerns about global warming, scientists are looking for potential renewable energy sources. Fossil fuels are
being depleted and produce a by-product, carbon dioxide, which is a likely contributor of global warming [1]. There is a need to find alternative forms of energy. Some alternative energy sources such as water or wind are limited to areas with windy environments or flowing rivers. Utilizing energy from the sun allows all parts of the world to use this energy. Solar power from solar cells is not only environmentally safe, but also use as energy source that will exist for billions of years. The solar cell with the highest efficiency currently, 25%, is a silicon pn junction solar cell [2]. The problem with these solar cells is its high cost to make. The basic mechanism of a DSSC is the conversion of light energy into electrical energy. In a DSSC, sunlight strikes the dye and excites an electron in a higher molecular orbital. The electron in the higher molecular orbital of the dye is then injected into the conduction band of the semi-conductor (usually titania or zinc oxide). The electron passes from the semiconductor to the electrode and creates a current that drives the work for the system. The electron then routes to the counter electrode and combines with the electrolyte. The electrolyte consists of organic solvent containing an iodide/triiodide redox system. Specifically, the electron from the counter electrode converts triiodide in the electrolyte into iodide. The iodide becomes triiodide again by donating one of its electrons into the empty orbital of the dye, which can in turn be excited by sunlight and injected into the semiconductor. This process occurs quickly and results in no net chemical change [3]. There are many factors that affect the efficiency of the DSSC. An efficient DSSC requires: (1) a dye with efficient electron injection into the semiconductor, (2) an electrolyte able to penetrate into the porous semiconductor to efficiently reduce oxidized dye molecules, (3) a semiconductor with a large surface area for maximum dye adsorption, and (4) a long diffusion length (fast electron transport) for the injected electrons to be transported.[4].

In this article Dye-sensitized solar cells (DSSC) was fabricated by using natural dyes extracted from Lawsonia inermis leaf. *Lawsonia inermis* Linn (Family: Lythraceae) is a much branched glamorous shrub or small tree 2-6m in height, is leaves are cultivated for use in traditional medicine. Also this plant is a world wide known cosmetic agent used to stain hair, skin and nails [5]. The active constituent of the leaf is lawsone. The ‘Lawsone’ is principally responsible for the colourant property of the leaves and the structure is shown in Fig.1. [6].

The objective of this article is to fabricate DSSC using *Lawsonia inermis* Leaf and characterize the DSSC by using XRD and VIS spectrophotometer to obtain properties such as conversion efficiency, open voltage, fill factor, current density. The effect of adjusting pH values of the extracted Dye was also investigated.

![Figure 1: Structure of Lawsone](image-url)
Experimental
Preparation of Natural Dye Sensitizers
The methods used to extract the filtrate are cold ethanol extraction (A) and Soxhlet extractor with ethanol as the solvent (B). The extractions were obtained according to the following step: *Lawsoia inermis Leaf* was collected from Lagos state university farmlands site. The Fresh *Lawsoia inermis Leaf* was seasoned by drying them at room temperature in the laboratory for two-weeks, until they became invariant in weight; laboratory ceramic made pistle and mortal are then used to crush each dry specimen into tiny bits.

For the Soxhlet extractor with ethanol as the solvent (B), 25 gramme of each dried/crushed sample were weighed (using OHAUS Electronic weighing Balance Model Brainweight B1500 made in USA) and soaked in 250ml solution of ethanol in the soxhlet, this were heated with the heating mantle for six to eight hours until all the dye has being removed. The Solid residues were filtrated out to obtain clear dye solutions. The ethanol filtrate was placed in hot water bath for vaporization of the ethanol so as to concentrate the extract. The extract was allowed to cool. In the case of cold ethanol extraction (A), 25 gramme of each dried/crushed sample were weighed and soaked into 250ml solution of ethanol, these was left to age at room temperature in a dark place for 12 hours. The residual parts were later removed by filtration. The effect of extracting with (A) and (B) solvent was studied by a comparison of dyes extracted. Then, the phytochemical screening of the plant was done (test on the presence of anthraquinones and flavonoids), and the effect of pH of dye solution was studied by adjusting pH from the original pH using 0.1 M HCl solution to three different pHs (1.0, 2.0 and 3.0). The efficiency of the solar cells related to dye structures is discussed. The pH of the dye solution on the DSSC efficiency and stability were also determined.

Preparation and Construction of the Cell
The conductive glass plates (Fluorine-doped tin oxide glass sheet), with the sheet resistance 15ohm/cm, made by Solaronix SA were used. The FTO substrate (cut into 1.2x1.2cm² dimension) was used as a substrate for precipitating TiO₂. The TiO₂ was purchased from Aldrich. The TiO₂ solution was prepared by the incremental addition of 20 ml of nitric acid solution to 12 g of colloidal TiO₂ powder in a mortar and pestle while grinding (Degussa P25 TiO₂, 3500 Embassy Parkway, Akron, OH, 44333, USA or Degussa AG, D-6000, Frankfurt 11, Germany). Each 1 ml addition of the dilute acidic solution, proceeds only when the previous mixing and grinding has produced a uniform and lump-free paste. [6, 7]. The conductive glass sheet of 1.2x1.2cm² was immerged in isopropanol for 48h to remove any impurities. An adhesive plate was fixed on the four sides of conductive glass sheet to restrict the thickness and area of TiO₂. The titanium paste was spread on the conducting surface of the FTO slide glass. A glass rod is allowed to slide over the titanium dioxide suspension in order to spread evenly and smoothly. (9) It was annealed and sintered in an oven at 450°C for 30 min in order to solidify the TiO₂. The TiO₂-coated conductive glass is allowed to cool to room temperature. After cooling the TiO₂ film is stained with a dye solution for 24 h
to absorb the dye on TiO$_2$ porous film adequately. Platinum coated counter electrodes were prepared according to published procedures [8].

**Assembly of DSSC**
The DSSC was assembled by filling a liquid electrode (0.5M KI + 0.0M I$_2$) in solvent of ethylene glycol + acetonitrile with a volume ratio of 4:1 between a TiO$_2$ porous film electrode and the platinum coated counter electrodes. Two binder clips are used to gently hold the electrodes together at the edges.

**Measurement of Photoelectric Conversion Efficiency of DSSCs**
The crystalline phases of the TiO$_2$ film were identified by X-ray diffraction (sciece RAD-2R) using graphite monochromatized CuKα radiation ($\lambda = 0.154$nm).

The absorption spectra of dye solutions and dyes adsorbed on TiO$_2$ surface were recorded using a VIS Spectrophotometer (Spectrumlab 23A GHM Great Medical England). Solar energy conversion efficiency (the photocurrent voltage ($I-V$) curve) was measured by using digital multimeters under illumination of sunlight. Based on $I-V$ curve, the fill factor (FF) is defined as

$$\text{FF} = \frac{I_{\text{max}} \times V_{\text{max}}}{I_{\text{sc}} \times V_{\text{oc}}},$$  

(1)

where $I_{\text{max}}$ and $V_{\text{max}}$ denote the maximum output power current and voltage respectively, and $I_{\text{sc}}$ and $V_{\text{oc}}$ denote the short-circuit current and open-circuit voltage respectively. The total energy conversion efficiency ($\eta$) was defined as follows:

$$\eta = \frac{(I_{\text{sc}} \times V_{\text{oc}} \times \text{FF})}{P_{\text{in}}},$$  

(2)

where $P_{\text{in}}$ denote the energy of incident light.

**Results and Discussion**

Fig.2 shows the acquired absorption spectra of Lawsonia inermis leaf extract using (A) and (B), the two methods of extraction after UV illumination. As seen from the graph, the maximum absorption peak value for the leaf is at 800nm. Within this wavelength range the Lawsonia inermis leaf using (A) has higher absorption intensity than Lawsonia inermis leaf using (B). The difference in absorption intensity is due to the attachment of extract molecules to the surface of TiO$_2$ as shown in Fig.3. [9] Fig.4 compares the absorption spectra of lawsonia inermis leaf extract with the lawsonia inermis leaf extract mixed with TiO$_2$ nanoparticles using the two methods of extraction. We notice that after TiO$_2$ nanoparticles was added to the lawsonia inermis leaf extract, there is decrease in its absorption intensity from 400nm to 600nm and rises at wavelength 700nm to 800nm for the cold ethanol extract method. in the case of soxhlet ethanol extraction method there are two wavelength ranges, it increases from 400nm to 600nm and 700nm to 800nm. This property gives them better absorption since there is the DSSCs increase in charge transfer ability under normal sunlight.
Figure 2: The absorption Spectra of Lawsonia inermis Leaf Cold Ethanol Extraction (A) and soxhlet Ethanol Extraction (B)

Figure 3: Chelation Mechanism of Hydroxynaphthoquinone with TiO$_2$ particle.

Figure 4: compares the absorption spectrum of (A) Lawsonia inemis cold ethanol extraction with Lawsonia inemis leaf cold ethanol extraction + TiO$_2$ (B)Lawsonia inemis leaf soxhlet ethanol extraction with Lawsonia inemis leaf soxhlet ethanol extraction + TiO$_2$
Fig. 5-6 shows the XRD diffraction pattern of the TiO$_2$ thin film covered substrate obtained from the cold ethanol extraction (A) and Soxhlet extractor with ethanol as the solvent (B) and one notice that the XRD patterns exhibited strong diffraction peaks at 25° indicating TiO$_2$ in the Anatase phase not in amorphous phase, [10]

**Figure 5:** XRD diffraction pattern of the fabricated TiO$_2$ using the cold ethanol (C).

**Figure 6:** XRD Diffraction Pattern of the Fabricated TiO$_2$ Using the Soxhlet Extractor (D)

Fig. 7 shows the I-V curve of the prepared DSSC sensitized with Lawsonia inemis leaf using the cold ethanol extraction (A) and soxhlet extractor (B). The Lawsonia inemis leaf extracts using the soxhlet extractor (B) method results shows non-ideal I-V characteristics even though it possesses 100% light harvesting efficiency in the UV and in the visible parts of the electromagnetic spectrum. [11]
Fabrication of Dye-Sensitized Solar Cells (DSSC) Device

Figure 7: I-V curve of DSSC sensitized with lawsonia inermis leaf cold ethanol (A) and soxhlet ethanol extraction (B)

In Fig.8-9, the absorption spectrum of the irradiated TiO₂ nanoparticles adsorbed Lawsonia inermis leaf soxhlet extract is flat showing no light absorption in comparison with other method. This makes the DSC prepared not to function after a short period of operating. Whereas for the cold ethanol extraction (A) the DSSC still function for about 3 - 5hrs

Figure 8: Light Absorption spectra of Lawsonia inermis leaf cold ethanol extract (a) at pH 3.21 (b) adsorbed on TiO₂ at pH3.21 (c) at pH 3.0 (d) adsorbed on TiO₂ at pH3.0 (e) at pH 2.0 (f) adsorbed on TiO₂ at pH 2.0
Figure 9: Light Absorption spectra of Lawsonia inermis leaf soxhlet ethanol extract (a) at pH 3.21 (b) adsorbed on TiO₂ at pH3.21 (c) at pH 3.0 (d) adsorbed on TiO₂ at pH3.0 (e) at pH 2.0 (f) adsorbed on TiO₂ at pH 2.0

Table 1 shows the comparison of different parameters of DSSC’s using the natural dye extract. The photoelectric conversion efficiency of Lawsonia inermis leaf using (B) method is higher than the photoelectric conversion efficiency of Lawsonia inermis leaf using the (A) method. This is because extract adsorbed on the surface of TiO₂ nanoparticles has broad absorption wavelength range and high absorption intensity. The effect of pH values was also investigated in this paper. Table 2-3 shows that as pH value decreases from 3.0 to 1.0, the performance of DSSCs rises clearly, the photoelectric conversion efficiency of DSSCs is enhanced and it increases [12]. The phytochemical screening of the plant was done (test on the presence of anthraquinones and flavonoids). We observed the presence of less anthraquinones and no flavonoids when using method (B), but the presence of flavonoids and less anthraquinone with method (A). This might be the reason for the loss of photoelectric conversion efficiency [3].

Table 2

<table>
<thead>
<tr>
<th>Extracting solvent</th>
<th>Extract</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm²)</th>
<th>η%</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>cold ethanol</td>
<td>Lawsonia inermis leaf</td>
<td>0.302</td>
<td>0.82</td>
<td>0.349</td>
<td>0.659</td>
</tr>
<tr>
<td>soxhlet ethanol</td>
<td>Lawsonia inermis leaf</td>
<td>0.072</td>
<td>0.94</td>
<td>0.677</td>
<td>0.828</td>
</tr>
</tbody>
</table>
Table 3: Effect of pH on lawsonia inermis leaf extract solution (cold ethanol solvent)

<table>
<thead>
<tr>
<th>pH</th>
<th>V_{oc}(V)</th>
<th>I_{sc}(mA/cm^2)</th>
<th>η%</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.21</td>
<td>0.302</td>
<td>0.82</td>
<td>0.349</td>
<td>0.659</td>
</tr>
<tr>
<td>3</td>
<td>0.302</td>
<td>0.84</td>
<td>0.3577</td>
<td>0.707</td>
</tr>
<tr>
<td>2</td>
<td>0.304</td>
<td>0.86</td>
<td>0.3688</td>
<td>0.771</td>
</tr>
<tr>
<td>1</td>
<td>0.306</td>
<td>0.9</td>
<td>0.3902</td>
<td>0.806</td>
</tr>
</tbody>
</table>

Table 4: Effect of pH on Lawsonia Inermis Leaf Extract Solution (soxhlet Ethanol Solvent)

<table>
<thead>
<tr>
<th>pH</th>
<th>V_{oc}(V)</th>
<th>I_{sc}(mA/cm^2)</th>
<th>η%</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>0.072</td>
<td>0.94</td>
<td>0.677</td>
<td>0.828</td>
</tr>
<tr>
<td>3</td>
<td>0.074</td>
<td>0.94</td>
<td>0.531</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>0.075</td>
<td>0.96</td>
<td>0.550</td>
<td>0.875</td>
</tr>
<tr>
<td>1</td>
<td>0.076</td>
<td>0.98</td>
<td>0.569</td>
<td>0.901</td>
</tr>
</tbody>
</table>

Conclusion

The DSSC of reasonably high efficiency can be developed using Lawsonia inermis extracts using different solvents. The result for extracts using cold ethanol was slightly better than that of extract obtained using a soxhlet ethanol extractor. The efficiency obtained under long time irradiation period confirmed a reduction in value of efficiency for DSSC prepared with cold ethanol compared with that constructed using soxhlet ethanol extractor. Therefore in terms of long period stability in efficiency of DSSC, ethanol could be considered to be suitable as solvent for the extraction of natural dye used as sensitized in DSSCs. The XRD diffraction pattern of the TiO₂ thin film covered Lawsonia inermis substrate obtained from the extraction solvents exhibited strong diffraction peaks at 25° indicating TiO₂ in the Anatase phase. The absorption spectra of Lawsonia inemis extract mixed with TiO₂ nanoparticles using the two methods give better absorption property for (A), since there is increase in charge transfer under normal sunlight for the DSSCs and the maximum acquired after UV illumination is 800nm. The I-V curve of the prepared DSSC sensitized extracts using the soxhlet extractor (B) shows non-ideal I-V characteristics and there is increase in efficiency as pH decreases.

References


[8] Giuseppe Calogero, Gaetano Di Marco, Silvia Cuzzanti, Stefano Caramori, Robert


